PATENT SPECIFICATION

NO DRAWINGS

872,149

Date of Application and filing Complete Specification: March 7, 1958.

No. 7356/58.

Application made in France on Sept. 2, 1957.

Complete Specification Published: July 5, 1961.

Index at acceptance:—Classes 95, A(3:5); and 1(3), A1D(8:45), A1G(46D8:46D45:47D8:

CORRECTION OF CLERICAL ERROR

SPECIFICATION NO. 872,149

The following correction is in accordance with the Decision of the Assistant Comptroller acting for the Comptroller-General, dated the 27th day of March 1963.

Page 1, line 1, *after* "We" *insert* "Omya S.A. a French Body Corporate, organised under the laws of the French Republic of 30, Rue Saint-Augustin, Paris, France, formerly"

THE PATENT OFFICE
2nd May 1963

DS 72992/1(11)/R.109 200 4/63 PL

used as paint or a compounded plastic (polyvinyl chloride or polyester plus a filler) contains a percentage of filler of the order of 20 to 40%, the degree of whiteness of the filler has an important influence on the tint of the finished product. Thus it is impossible to obtain a pure white if the filler itself is not perfectly white.

The obtaining of very white fillers requires very pure raw materials containing the least possible amount of impurities having a basis of iron or other metals. It is therefore necessary to employ either products purified or perpared by chemical methods, as for example precipitated calcium carbonates, or natural raw materials of very high purity.

Difficulties arise in both of these cases, namely

1. the products obtained by chemical methods are too costly for current uses and have a very high oil absorption coefficient;

2. very pure natural products (carbonates, sulphates, alkaline earth silicates) are always of a crystalline structure. That is to say they have great hardness, whence difficulties of grinding arise as well as inconveniences due to their abrasive properties. Moreover, natural crystalline products have a very weak hiding power.

The present invention has for its object, in particular, a process allowing improved fillers

3. Intake of oil:
It should be as low as possible

4. Hiding power:
It should be as high as possible without it being necessary to attain the values obtained with pigments of high refractive idices.

A feature of the invention consists in a process in which fine particles of a mineral filler material as hereinafter defined are treated at the same time, in the absence of water, with extremely fine particles of a white pigment of high refractive index, and with a carboxylic or sulphonic acid of the aliphatic or aromatic series.

The term "mineral filler material" throughout this specification is intended to include mineral materials hitherto largely used in this capacity such as the various types of calcium corbonates, calcium sulphate, barium carbonate, other alkaline earth sulphates (for example barium sulphate), magnesium carbonate, dolomites, kaolins, silicas, micas, talcs and the like.

By fine particles is meant, so far as the mineral filler material is concerned, particles which, on the average, do not have a dimension greater than 10 microns and, in practice have a dimension of the order of 5 to 7 microns; of course, finer particles may also be used but below 3 microns on the average the

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International Classification:—C09d. C09c.

COMPLETE SPECIFICATION

Improved Fillers and their preparation

We, SOCIETE ANONYME DU BLANC OMYA, a French Body Corporate, organised under the Laws of the French Republic of 31, rue Cambaceres, Paris, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

In the paint and plastic industries there is an ever increasing demand for fillers of perfect whiteness and having by reason of their opacity as high a hiding power as possible with the object of obtaining finished products having beautiful clear and fresh tints.

When the mixture which is intended to be used as paint or a compounded plastic (polyvinyl chloride or polyester plus a filler) contains a percentage of filler of the order of 20 to 40%, the degree of whiteness of the filler has an important influence on the tint of the finished product. Thus it is impossible to obtain a pure white if the filler itself is not perfectly white.

The obtaining of very white fillers requires very pure raw materials containing the least possible amount of impurities having a basis of iron or other metals. It is therefore necessary to employ either products purified or perpared by chemical methods, as for example precipitated calcium carbonates, or natural raw materials of very high purity.

Difficulties arise in both of these cases, namely

1. the products obtained by chemical methods are too costly for current uses and have a very high oil absorption coefficient;

2. very pure natural products (carbonates, sulphates, alkaline earth silicates) are always of a crystalline structure. That is to say they have great hardness, whence difficulties of grinding arise as well as inconveniences due to their abrasive properties. Moreover, natural crystalline products have a very weak hiding power.

The present invention has for its object, in particular, a process allowing improved fillers to be obtained, which possess to a high degree the ideal properties required by industry, with the employment of means which are less costly and which give rise to less difficulties than the means utilised up to the present.

The properties which an ideal filler should possess are as follows:

1. Fineness:

According to the applicants envisaged the mean statistical diameter of the particles should lie between 1 micron and 7 microns.

2. Whiteness:

It should approach as closely as possible to that of chemically pure magnesium carbonate, considered as the standard of whiteness.

3. Intake of oil:

It should be as low as possible

4. Hiding power:

It should be as high as possible without it being necessary to attain the values obtained with pigments of high refractive idices.

A feature of the invention consists in a process in which fine particles of a mineral filler material as hereinafter defined are treated at the same time, in the absence of water, with extremely fine particles of a white pigment of high refractive index, and with a carboxylic or sulphonic acid of the aliphatic or aromatic series.

The term "mineral filler material" throughout this specification is intended to include mineral materials hitherto largely used in this capacity such as the various types of calcium corbonates, calcium sulphate, barium carbonate, other alkaline earth sulphates (for example barium sulphate), magnesium carbonate, dolomites, kaolins, silicas, micas, talcs and the like.

By fine particles is meant, so far as the mineral filler material is concerned, particles which, on the average, do not have a dimension greater than 10 microns and, in practice have a dimension of the order of 5 to 7 microns; of course, finer particles may also be used but below 3 microns on the average the

process loses one of its advantages, in particular the possibility of employing a standard grinder, although the other advantages are not not thereby compromised.

The extremely fine pigment particles are particles the mean dimension of which is distinctly less than that of the mineral filler material particles, for example a dimension of 0.1 micron or less.

The invention is of particular interest in the treatment of calcium carbonates of the calcite type and, for this reason, the description which follows refers above all to these materials, nevertheless, the invention is applicable to all the other known mineral filler materials which are specified above.

In order to obtain a sufficient hiding power with hard and crystalline natural products, it is necessary to reduce them to a very great degree of fineness of the order of from 1 to 3 microns.

This involves practical difficulties since elaborate grinding operations contaminate the product by contact with the metallic grinding surfaces and considerably alter the whiteness. Finenesses of 1 to 3 microns can only be achieved, without imparting a grey tint to the product, by the employment of very costly processes employing jet-mills or Fluid-energy-mills and using the principle of mutual friction of the particles themselves. Another process consists in effecting the grinding by a wet method, but this implies important and costly installations and leads to a relatively high cost price.

According to the present process, the crystalline mineral filler material is, on the contrary, ground by a dry method to a degree of fineness which has no need to be very high but which is sufficient to ensure good properties in the paints and presents the advantage of a low oil intake. On the other hand, the hiding power is obtained by the treatment defined above which produces a coating on a core of mineral filler material of a white pigment of high refractive index.

In this respect it has already been proposed to coat fine particles of natural calcium carbonate either with fatty acids or with very fine particles of pigments of high refractive index, such as titanium oxide. In the latter case it is a question of the direct fixation of the pigment particles on the particles of the mineral filler material.

According to the present process the treatment is effected, on the contrary, with aliphatic or aromatic carboxylic or sulphonic acids and with pigments of high refractive index at the same time.

The importance and interest of the new process are that benefits accrue from the advantages of a moderate grinding in known grinding apparatus and the advantages inherent in a low intake of oil. In addition the hiding power may be modified as desired.

Moreover, the coating of the particles of mineral filler material by the white pigment causes an increase of the hiding power greater than that which is obtained if this same quantity of pigment is added alone, that is to say without acid.

In order to obtain a permanent and homogeneous fixing of the pigment particles on to a core of mineral filler material (for example, core particles having a size of 5 to 6 microns) several problems present themselves which have been resolved by the process described hereinafter.

1. Choice of the white pigment.

Generally speaking, any white pigment whatsoever may be chosen which has a refractive index which is higher than that of the mineral filler material. There is advantage, however, in choosing a pigment of high hiding power with the object of being able to use it in small quantity in relation to the mineral filler material. On the other hand, experience proves that, in order to obtain a good coating, there is advantage in the mineral filler material and the pigment possessing a mutual physico-chemical affinity.

In this respect, it is recommended to employ, as the mineral filler material, very pure calcium carbonate of the calcite type and, as the pigment material, titanium dioxide TiO_2.

Calcium carbonate possesses a slight natural alkalinity whilst titanium dioxide is an acid anhydride (titanic acid). There is thus affinity between these two products and, as a consequence, the hiding power of the titanium dioxide is raised to such a degree that it can be used in very small proportion in relation to the mineral filler material. This affinity between the calcium carbonate and the titanium dioxide constitutes one of the important advantages of the invention.

2. Physical properties of the pigment employed.

In order to obtain an efficient coating, it is necessary that, for each carbonate particle, there is a much larger number of titanium dioxide particles. It is therefore necessary that the pigment should be much finer than the mineral filler material. If calcium carbonate having a mean particle diameter of 6 microns is used as starting material, experience shows that the titanium dioxide must have a fineness of at least 0.1 micron. In this case with the object of obtaining a hiding power distinctly greater than that of expensively ground mineral filler materials having a mean diameter of 1 to 3 microns, it is sufficient to effect the coating of the core of $CaCO_3$ in the proportion of 1% by weight of TiO_2 for 99% of $CaCO_3$.

Much higher percentages may be used, however, for example up to 10% of the pigment.

It is simple to verify by calculation that, for the proportions of 1% and 99% indicated

process loses one of its advantages, in particular the possibility of employing a standard grinder, although the other advantages are not not thereby compromised.

The extremely fine pigment particles are particles the mean dimension of which is distinctly less than that of the mineral filler material particles, for example a dimension of 0.1 micron or less.

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Much higher percentages may be used, however, for example up to 10% of the pigment.

It is simple to verify by calculation that, for the proportions of 1% and 99% indicated

above and for dimensions of 0.1 and 6 microns for the particles of TiO_2 and $CaCO_3$, respectively, the pigment contains 1500 times more particles than the mineral filler material.

For carrying out the process according to the invention there is advantage in operating by grinding the filler material, in particular calcite, to reduce it to particles of the mean dimension desired, in the simultaneous presence of the carboxylic or sulphonic acid and of the pigment in particles already having the desired fineness.

It has been proved that there is advantage in carrying out the grinding at a higher temperature than normal, preferably at a temperature of from 50 to 80°C. Preferably the temperature is selected so that at that temperature the actual organic acid used is sufficiently fluid to bring about a uniform dispersion of pigment particles. It is recommended to raise the mineral filler material to a temperature of this order before its introduction into the grinder.

The acid used may be a saturated or nonsaturated higher fatty acid, an aromatic acid, a dibasic acid, a hydroxy acid or an organic sulphonic acid. Among the acids capable of being used mention may be made in particular of stearic acid, oleic acid, lauric acid, and abietic acid, polyacids such as oxalic and maleic acids, and hydroxy acids such as lactic acid and ricinoleic acid; likewise there may be used adipic acid, salicylic acid, benzoic acid and naphtholsulphonic acid.

Such acids have, by themselves, a strong chemical affinity for the carbonate, particularly if the treatment is effected at a temperature of 50 to 80°C or more. There is then obtained a simultaneous fixation of the organic acid and the particles of titanium dioxide on the carbonate particles, which forms a kind of lacquering.

In other words, the organic acid performs the role of vehicle and fixer for the titanium dioxide. The organic acid becomes fixed on the core of the mineral filler material by absorption and chemical reaction.

The smallest proportion of organic acid that may be used for the treatment in relation to the carbonate is 0.5%; it may reach 10% in the case of fatty acids of the stearic and oleic type for example.

The following Example illustrates the process used:

EXAMPLE

Calcium carbonate of the calcite type is ground in a hammer mill or edge mill at a temperature of 50 to 80°C. There is introduced at the same time, into the mill, a mixture of equal weights of titanium dioxide (0.1 micron) and stearic acid, this mixture being added to the mill at the rate of 1.5 to 2% by weight in relation to the calcium carbonate.

The grinding is continued (continuously or intermittently) until the particles of carbonate are reduced to a mean diameter of 5 to 7 microns.

The product resulting from this process has the following advantages:—

Intake of oil: 15% (rub-out test), enabling brilliant paints to be obtained.

Hiding power higher than that obtained with the same carbonate untreated, reduced to a fineness of 1 to 3 microns by the employment of a Jet-Mill, or by wet grinding.

Paints in which the filler material thus prepared has been incorporated offer the advantages, amongst others, of providing films of high hiding power, of great hardness and of an excellent resistance to ageing.

It is interesting to notice that the efficiency of the coating of the core by the acid is such that the same properties cannot be obtained by adding the carbonate, the acid and the pigment directly to paints.

In addition, the process enables the manufacture of a white filler having all the ideal properties with a view to its addition to paints or to plastic materials by the operation of a simple and inexpensive apparatus, although, up to the present, the best results, distinctly inferior to those obtained by the present invention, could only be ensured by very complicated and costly processes.

The fillers prepared according to the invention may be incorporated in paints, compounded plastic materials and the like by processes used or proposed up to the present for the incorporation of untreated fillers. The products thus obtained form part of the present invention.

WHAT WE CLAIM IS:—

1. A process for the production of an improved filler in which fine particles of a mineral filler material as hereinbefore defined are treated at the same time, in the absence of water, with extremely fine particles of a white pigment of high refractive index and with a carboxylic or sulphonic acid of the aliphatic or aromatic series.

2. A process as claimed in claim 1, in which the treatment is effected by grinding the mineral filler material into particles of a mean dimension not exceeding 10 microns, in the presence of the acid and of the pigment, the particle size of the pigment having a mean dimension not exceeding 0.1 micron.

3. A process as claimed in claim 2, in which the mean dimension of the particles of mineral filler material after grinding are between 3 and 10 microns.

4. A proces as claimed in claim 2 and 3, in which the grinding is carried out at a temperature of from 50 to 80°C.

5. A process according to claim 4, in which the mineral filler material is raised to a temperature of from 50 to 80°C prior to being ground.

6. A process according to any one of the

preceeding claims, in which the acid is used in a proportion of up to 10% in relation to the weight of the mineral filler material.

7. A process for the preparation of a filler substantially as described in the foregoing Example.

8. A filler when obtained by the process claimed in any one of claims 1 to 6.

9. A filler consisting of fine particles, each comprising a core of a calcium carbonate of the calcite type coated with extremely fine particles of a white pigment of high refractive index fixed on the core by treating the core at the same time, and in the absence of water, with extremely fine particles of a white pigment of high refractive index and with a carboxylic or sulphonic acid of the aliphatic or aromatic series.

10. A filler as claimed in claim 9, in which the mean dimension of the cores is between 3 and 10 microns and in which the mean dimension of the particles of white pigment does not exceed 0.1 micron.

11. A filler prepared substantially as described in the foregoing example.

12. Paint and plastic material containing the filler specified under claim 8, 9, 10 or 11.

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